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METALS AND NUTRIENTS IN THE SEDIMENTS OF SMALL LAKES IN KUUSAMO, NORTH-EASTERN FINLAND

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The aim was to investigate nutrients and metals in the sediments of small lakes in the Koutajoki river basin and improve our knowledge of the watercourses in Kuusamo. The lakes were in a natural state without any direct human interference. The bedrock was very variable. Metal concentrations were usually highest in the areas overlying basic rocks and till deposits. The pH of the sediments was quite high due to the basic rocks and basic dykes in the catchment areas overlying silicious rocks. Sulphide mineral deposits caused probably some anomalous high metal concentrations. There were correlations between most metals, which seemed to behave similarly and migrate towards the surface of the sediments. A human effect may have been the cause of high lead, zinc, cadmium and mercury concentrations in some cases. Cadmium concentrations were low and indicated less anthropogenic effect than in reference areas in Central Finland and North America. Morphometric factors associated with the lakes and the physiography of the catchment area affected the organic matter content and the precipitation of phosphorus, lead, manganese and nickel.

Index words: Sediment, bedrock, soil, lake, metals, trace elements, nutrients, Kuusamo

1. INTRODUCTION

Lake sediments are studied for many purposes. Stratigraphical observations provide information on the history of the lakes and possible changes in loading by waste water or airborne deposits. The interaction between sediments and water is a further object of study, and sediments can also be used in geochemical prospecting. In recent years acid rain and the increase in metals in lakes and rivers have become a very serious problem, and sediments may prove better indicators than water itself, although more research still needs to be devoted to the interactions between air, soil, water and sediments. We need also more information about watercourses which are in a natural state and about the very complicated geochemical and biochemical reactions which take place in them.

The lakes and rivers of the present research area, the Koutajoki river basin in Kuusamo (Figs 1—2), are assumed to be largely in a natural state, although affected by atmospheric deposition of acids and other substances. With the latter in mind, research is urgently needed to establish background values for the water quality in the area. The earlier history of this basin can be seen in the vertical stratification of the sediments, and this also helps

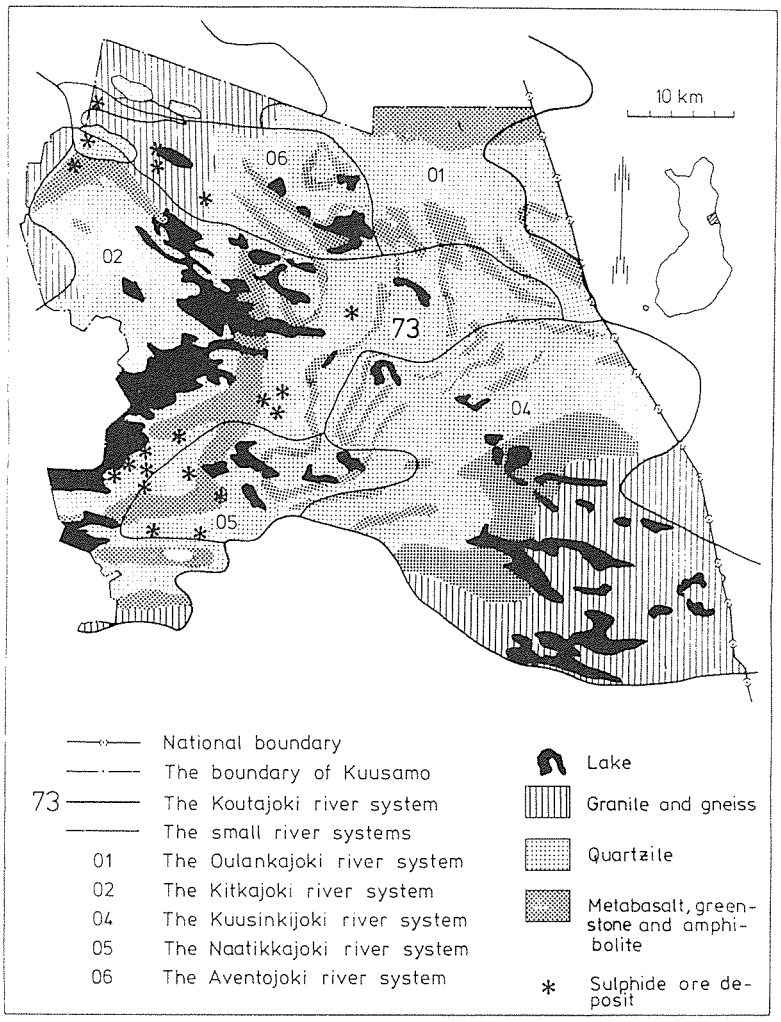

Fig. 1. Bedrock of the study area.

to separate the effect of anomalous metal concentrations in the bedrock from the atmospheric effects.

The area (Fig. 1) falls mostly within the Karelidic schist Belt (Simonen 1980), typical rocks being conglomerates, quartzites, phyllites, dolomites and limestones. There are also dykes, lava beds and greenstones in the sedimented rocks (Piispanen 1972), and many mineralisations have also been identified, containing cobalt, copper and gold (Pankka and Vanhanen 1984). Heavy metals occur in the form of pyrites and albitites, for instance (Piispanen 1972, Lahermo et al. 1979). The northeast part of the area forms part of the basement gneiss complex of Eastern Finland, in which the most common rocks are trondhjemites, granite gneisses and granodiorites. There are also diabase dykes (Piispanen 1972).

The water quality of the lakes in Kuusamo has been earlier discussed e.g. by Heinonen and Myllymaa (1974), Myllymaa (1978), Myllymaa and Ylitolonen (1980) and Piispanen and Myllymaa (1982), and the lakes referred here have been studied earlier by Myllymaa (1985). Myllymaa et al. (1985) have studied nutrient and metal concentrations in the Kitkajärvi chain of lakes.

The purpose of the present work was to investigate the concentrations of nutrients and metals in the sediments of the small lakes and the factors affecting their vertical and spatial variations. A further general aim was to improve our knowledge of the watercourses in this area.

2. MATERIAL AND METHODS

The sediment samples were collected from 41 small lakes and one larger lake (Kangerjärvi; Fig. 2) in November and December 1983. The lakes, which varied in area in the range 0.1—0.49 km^2, were not loaded by waste water. The samples were taken using a Hakala-type Kajak sampler (see Hakala 1971) and were each 5 cm in diameter and about 30 cm long.

The sediment profiles were cut into three parts, 0—10, 10—20 and 20—26 cm, measuring from the surface. pH, residue and loss on ignition, total nitrogen and total phosphorus were analysed at the laboratory of the Water District Office of Oulu. The methods used for analysing nitrogen and phosphorus are described in the report of Nordforsk, Miljövårdssekretariatet (1975). The samples were dried in 70°C and ashed for 4—6 hours at 550°C.

Lead, copper, zinc, iron, manganese, molybdenum, cobalt and nickel were determined at the regional laboratory of the Geological Survey of Finland in Rovaniemi. Ash was extracted for one hour at 110°C and the concentrations were measured by AAS. The sensitivity limit of the assay for molybdenum was 5 mg kg^{-1} and that for the other metals 6 mg kg^{-1}.

Cadmium concentrations in the ash were determined at the Water Technology Laboratory of Oulu University by the AAS method with a sensitivity limit of 0.01 mg kg^{-1}. Mercury concentrations in 15 lakes were determined at the Research Laboratory of the National Board of Waters using the cold vapour AAS technique after wet combustion (Amstrong and Uthe 1971). The results were given as concentrations of dry matter.

The sediments of two lakes (nos. 90 and 94; Fig. 2) were studied in more detail by dividing the samples into 2 cm sections for chemical analysis and 1 cm sections for Pb-210 dating. The samples for dating were freeze-dried and homogenised and the Pb activity present at each depth determined by

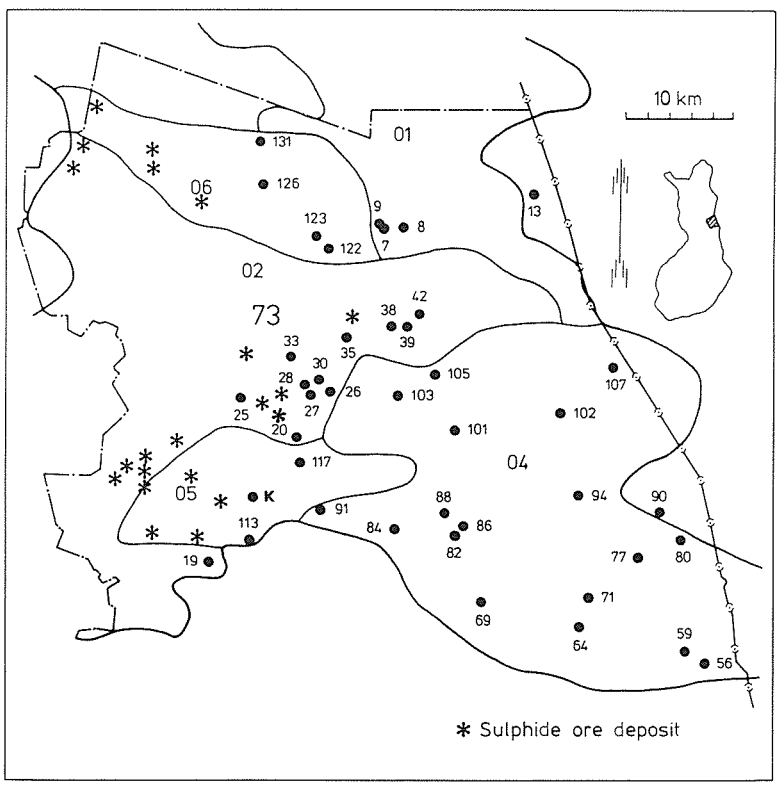

Fig. 2. Study area, observation stations and explored sulphide ore deposits. The numerical symbols of lakes equal to those reported by Myllymaa (1985) besides K (Kangerjärvi).

measuring the activity of Po-210 cf. (Rekolainen et al. 1986). Age and sedimentation rate were calculated using C.I.C. (constant rate of supply) models (Robbins and Edgington 1975, Appleby and Oldfield 1978).

The bedrock of the area was grouped into three classes according to chemical composition (see Myllymaa 1985): silicious (class 1), basic (class 2) and intermediate (class 3; cf. Huang 1962, Lahermo 1970, Rönkä et al. 1980 and Rönkä 1983). The soil classes were: sand or gravel (class 1), till (class 2), till with peat deposits (class 3) and peat in the main catchment area (class 4).

3. RESULTS

3.1 Organic matter, sedimentation rate and pH

Loss on ignition (Fig. 3), indicating the organic matter content of the sediment, varied in the range 26.0—70.2 %, with a mean of 42.8 % (s = 9.8 %; Table 1). The vertical variation was small. The lowest values were recorded in the area where the lakes were shallowest and the percentage of lakes smallest, since organic matter sinks more slowly than inorganic. Loss on ignition correlated negatively with total depth and the area of the catchment basin (Table 2) and showed marginal positive correlations with the percentages of peatlands and lakes in the catchment area.

The average sedimentation rate (Fig. 3) in Lake Yli-Heikinjärvi (no. 90; Fig. 2) has been 15 mg cm^{-2} a^{-1} over the last 100 years, and that in Lake Särkijärvi (no. 94; Fig. 2) 17 mg cm^{-2} a^{-1}. Sedimentation was most rapid in the former about 50 years ago (24 mg cm^{-2} a^{-1}) and in the latter about 65 years ago (17 mg cm^{-2} a^{-1}). The sediments of these lakes were quite similar in structure, the most important difference being their total depth.

Because of the decrease in dry matter towards the surface, the density increased towards the deeper layers. Growth of the thickness of the sediments in these two lakes has been 2.3—2.4 mm a^{-1} on average, compared with 3.0—3.3 mm a^{-1} (Granberg 1985) in the lakes on the upper part of the Iijoki river and 2.0 mm a^{-1} since 1962 in the eutrophic Lake Torankijärvi in Kuusamo (Kainua 1985).

The spatial variation in pH (Fig. 3) in the sediments was great, with a mean value of 6.0 (s = 0.7; Table 1). The significant negative correlation between pH and loss on ignition (Table 2) was due to organic acids (cf. Tuokko 1980).

pH correlated very significantly with the area of the catchment basin, and the differences between the soil classes 1/2 and 1/3 and the rock classes 1/2 were almost significant, the highest values recorded in the areas with till soils and basic rocks.

Table 1. Mean values, standard deviations (S), maxima and minima for the variables in dry matter and ash with respect to the whole sediment cores. Number of observations is 41 except 15 for mercury. pH measured from fresh sediment in the laboratory.

Variable		Dry matter				Ash			
		Mean	S	Min.	Max.	Mean	S	Min.	Max.
Residue on ign.	%	59.9	19.0	30.0	116.0				
Loss on ign.	%	42.8	9.8	26.0	70.2				
pH		6.0	0.7	4.2	7.5				
Nitrogen	mg g^{-1}	17.2	4.9	9.1	26.9				
Phosphorus	mg g^{-1}	2.9	1.8	0.9	8.3				
Lead	mg kg^{-1}	18.0	6.0	4	34	32.9	15.6	6	100
Copper	mg kg^{-1}	37.5	91.2	4	593	65.4	142.8	8	920
Zinc	mg kg^{-1}	89.6	37.0	32	181	162.0	75.7	50	408
Cadmium	mg kg^{-1}	0.32	0.15	0.12	0.85	0.58	0.33	0.16	1.56
Mercury	mg kg^{-1}	0.137	0.088	0.03	0.40				
Iron	mg g^{-1}	101.2	91.6	2	450	177.2	151.8	3.4	740
Manganese	mg g^{-1}	6.1	15.6	0.1	77.6	9.2	21.8	0.2	104
Molybdenum	mg kg^{-1}	4.7	3.5	0	16.0	7.9	5.2	0	25
Cobalt	mg kg^{-1}	24.2	38.2	3	251	41.1	58.3	6	388
Nickel	mg kg^{-1}	16.7	8.5	3	43	29.8	15.5	6	72

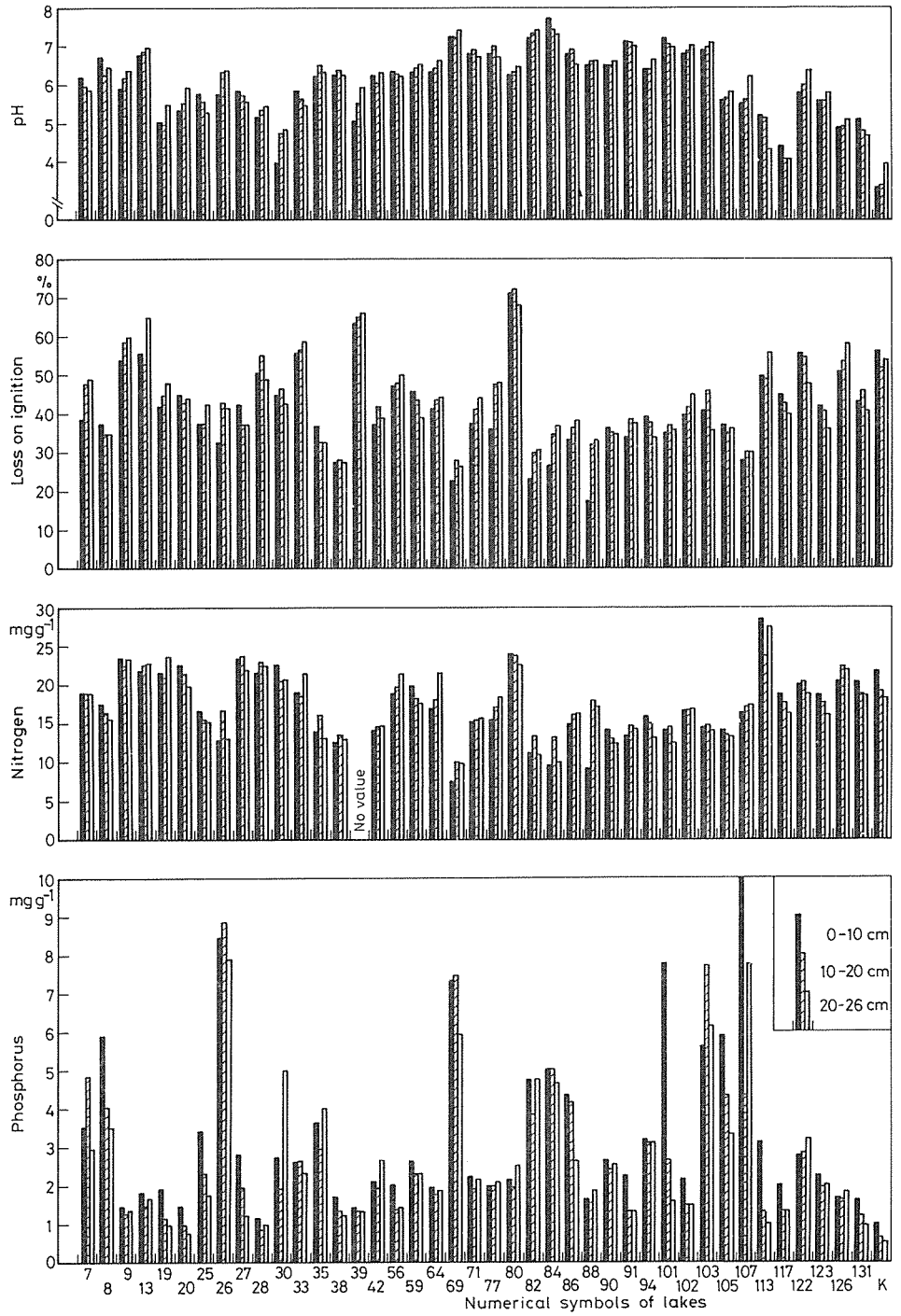

Fig. 3. Vertical distribution of loss on ignition, pH, nitrogen and phosphorus in dry matter. The numerical symbols of the lakes equal to those in Fig. 1.

3.2 Nitrogen and phosphorus

Mean nitrogen concentration was 17.2 mg g^{-1} of dry matter (Table 1). Nitrogen concentration showed a highly significant correlation with loss on ignition (Table 2) and a negative one with pH due to the binding of nitrogen to organic material. There were no significant differences between the different parts of the sediments in this respect (Fig. 3). Like organic matter, nitrogen correlated negatively with the total depth of the lake and the area of the catchment basin (Table 2).

The mean concentration of phosphorus was 2.9 mg g^{-1} (Table 1). The vertical variation was not statistically significant, but was very great in some lakes (Fig. 3). Phosphorus correlated negatively with loss on ignition and nitrogen and almost significantly with pH (Table 2), so that it also correlated with total depth. There was a significant difference in phosphorus concentration between soil classes 2/4 and 3/4, the highest values being found in the areas of till soils, class 2.

3.3 Metals

3.31 Lead

The mean concentration of lead was 18.0 mg kg^{-1} of dry matter or 32.9 mg kg^{-1} of ash (Table 1). The vertical variation (Fig. 4) was great and statistically highly significant, the highest concentrations (mean 53.4 mg kg^{-1}) being found in the upper parts of the sediments (Fig. 4). The variation was greatest in the upper parts (s = 25.9 mg kg^{-1}) and smallest in the lower parts (s = 9.9 mg kg^{-1}).

There was a highly significant correlation between lead and loss on ignition (Table 2), which suggested that lead had become enriched in the organic material. Hence it correlated negatively with the area of the catchment basin (Table 2). It also correlated with Zn, Cd and the Fe/Mn ratio.

Table 2. Correlations with statistical significance ($p < 0.1$) between the variables. Degrees of uncertainty: ° 10 %; * 5 %; **1.0 %; *** 0.1 %; — no correlation. LOI = loss on ignition; A = area of lake; F = area of catchment basin; Peat = percentage of peatlands; L = percentage of lakes.

	LOI	pH	N	P	Pb	Cu	Zn	Cd	Hg	Fe	Mn	Fe/Mn	Mo	Co	Ni
pH	.390 **														
N	.519 ***	−.422 **													
P	−.435 **	.316 *	−.430 **												
Pb	625 ***	—	—	—											
Zn	.400 **	.323 *	—	—	.488 ***	—									
Cd	.538 ***	—	—	—	.661 ***	—	.670 ***								
Hg	−.265 °	.447 ***	−.408 °	.578 *	—	.847 ***	—	—							
Fe	—	—	—	—	—	.270 °	—	—	—						
Mn	−.358 *	.436 **	−.381 *	.615 ***	—	—	—	—	—	—					
Fe/Mn	.686 ***	−.356 *	—	.410 **	.554 ***	—	—	—	—	—	−.366 *				
Mo	—	.289 °	−.319 *	.398 **	—	—	.327 *	—	—	—	—	—			
Co	—	—	—	.276 °	—	.940 ***	—	—	.849 ***	.356 *	—	—	.433 **		
Ni	−.358 *	—	—	.287 °	—	.521 ***	.556 ***	.486 ***	.648 **	—	—	—	.315 *	.501 ***	
A	—	—	—	—	—	—	—	—	−.432 °	—	—	—	—	—	
Depth	−.317 *	—	−.305 *	.544 ***	—	—	—	—	—	—	.306	−.354 *	— *	—	.400 **
F	−.452 **	—	−.323 *	—	−.404 **	—	—	—	—	—	—	−.277 °	—	—	—
Peat	.288 °	—	—	−.288 °	—	—	—	—	—	—	—	.448 ***	—	—	—
L	.284 °	—	—	—	−.265 °	—	—	—	−.428 °	.431 **	—	.270 °	—	—	—

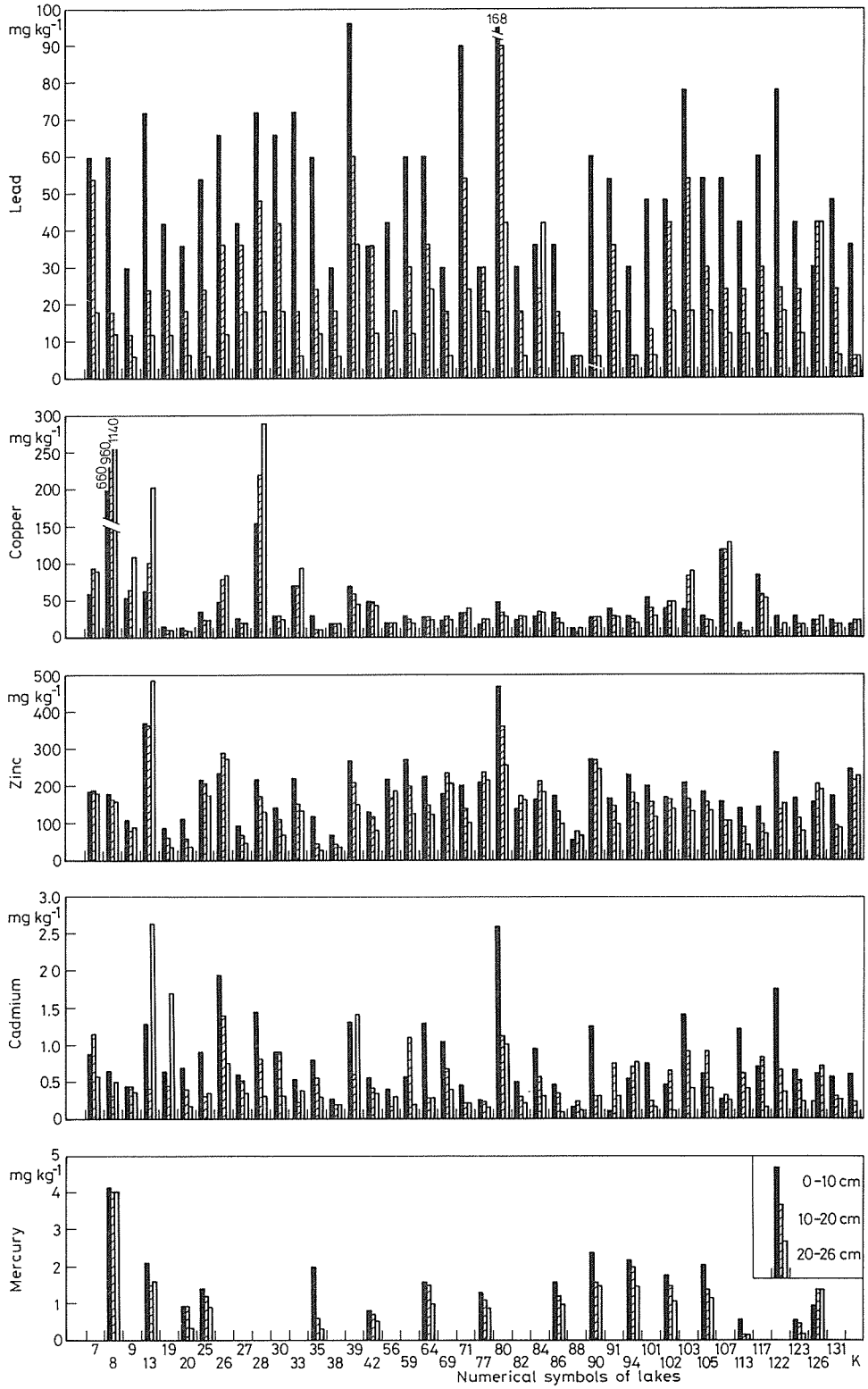

Fig. 4. Vertical distribution of lead, copper, zinc and cadmium in ash and mercury in dry matter.

3.32 Copper

The mean copper concentration in the sediment cores was 37.5 mg kg^{-1} of dry matter and 65.4 mg kg^{-1} of ash (Table 1), the values for some cores decreasing markedly towards the surface (Fig. 4). Copper correlated here with Hg, Mo, Co and Ni (Table 2). Some lakes (nos. 8, 9, 13, 18 and 107; Fig. 2) had anomalous high copper concentrations ($>$ 100 mg kg^{-1}), accompanied by high values for cobalt (Fig. 6), while the sediments of lake no. 8 were rich in zinc and mercury (Fig. 4). The highest mean value was recorded for rocks of class 2, but due an anomaly (max. 920 mg kg^{-1}) the differences were not significant.

3.33 Zinc

The mean concentration of zinc was 89.6 mg kg^{-1} of dry matter and 162.0 mg kg^{-1} of ash (Table 1). An increase could usually be seen towards the surface (Fig. 4), although this was not statistically significant due to the great variation in the upper part (Table 1). The highest values in this layer were in lakes 13 and 7 (Fig. 2), where the values for cadmium (Fig. 4) were also the greatest.

Zinc correlated with loss on ignition, Pb, Cd and Ni (Table 2), and seemed to be dependent more on organic matter than on Fe-Mn precipitates. The highest mean content (182.3 mg kg^{-1}) was in soil class 3, till and peat, the difference with respect to class 1 (mean 103.6 mg kg^{-1}) being almost significant.

3.34 Cadmium

The mean concentration of cadmium was 0.32 mg kg^{-1} of dry matter and 0.58 mg kg^{-1} of ash (Table 1). The values again increased towards the surface (Fig. 4), the difference being statistically highly significant. Cadmium correlated with loss on ignition, Pb, Zn and Ni (Table 2) and there was an almost significant difference in its concentration between soil classes 2 and 4, means 0.63 and 0.37 mg kg^{-1} respectively.

3.35 Mercury

The average dry matter concentration was 0.14 mg kg^{-1} (Table 1) with an increase towards the surface (Fig. 4) the corresponding values being 0.17 mg kg^{-1} in the upper part and 0.11 mg kg^{-1} in the lower part. Because of the small number of samples the difference was not statistically significant. The variation between the lakes was small (Fig. 4). Closer analysis of the sediments of Lakes Yli-Heikinjärvi (no. 90) and Särkijärvi (no. 94; cf. Rekolainen et al. 1986) showed the concentration to increase towards the surface in both cores, mostly in a linear manner, but with a greater increase at a depth of 6—8 cm corresponding in the Pb 210 dating to a time some 50—70 years ago, when sedimentation was also fastest. Mercury was correlated with pH, P, Cu, Mo, Co and Ni (Table 2).

3.36 Iron and manganese

The mean concentration of iron was 101 mg g^{-1} of dry matter and 177 mg g^{-1} of ash (Table 1), and that of manganese was 6.1 mg g^{-1} of dry matter and 9.2 mg g^{-1} of ash (Table 1). Iron concentration did not vary vertically as a rule (Fig. 5), but manganese increased usually towards the surface, and the vertical variation was great in some lakes (e.g. 8, 26, 69, 84 and 101; Fig. 5).

Iron was correlated only with the percentage of lakes, and weakly with cobalt (Table 2), while manganese was correlated with total depth, loss on ignition, pH, N, P and Mo (Table 2).

3.37 Molybdenum

The mean concentration of molybdenum was 4.7 mg kg^{-1} of dry matter and 7.9 kg^{-1} of ash (Table 1). Concentrations fell below the sensitivity limit of the assay method in lake no. 88 (Fig. 2), where the concentrations of lead, copper, zinc and cadmium were also very small (Fig. 4).

The concentrations did not vary much vertically (Fig. 6), except in lakes nos. 69 and 84, where the concentrations were high in the upper parts of the sediments. Manganese concentrations were also high in these parts of the sediments (Fig. 5).

Molybdenum was correlated with N (negatively), P, Zn, Cu, Mn, Co and Ni (Table 2).

3.38 Cobalt

The mean concentration of cobalt was 24.2 mg kg^{-1} of dry matter and 41.1 mg kg^{-1} of ash (Table 1). The vertical variation was usually small, but was more pronounced in certain lakes (Fig. 6). Concentrations were high in many lakes.

Cobalt was correlated with Cu, Hg, Fe, Mo and Ni (Table 2), and differed significantly between soil classes 1 and 3 the lowest mean value being found in the former (16 mg kg^{-1}) and the highest in the latter (53 mg kg^{-1}).

3.39 Nickel

The mean concentration of nickel was 16.7 mg kg^{-1} of dry matter and 29.8 mg kg^{-1} of ash (Table 1). The value usually increased towards the upper parts of the sediment (Fig. 6), but there were some lakes (nos. 13 and 26; Fig. 2) in which they were highest in the lowermost parts. These were also the lakes that had the highest overall values. Copper, mercury, iron, manganese and cobalt concentrations were also high in lake no. 8 (Figs. 4—6). Lake no. 13 contained high concentrations lead, copper, zinc and cadmium (Fig. 4) and lake no. 26 a very high concentration of phosphorus without any significant vertical variation (Fig. 3).

Nickel was correlated with Cu, Zn, Cd, Hg, Mo and Co (Table 2).

4. DISCUSSION

4.1 Organic matter, sedimentation rate and pH

The affinity of heavy metals for organic substances and their decomposition products is of great importance for the behaviour of trace substances in aquatic systems. Dissolved organic substances are

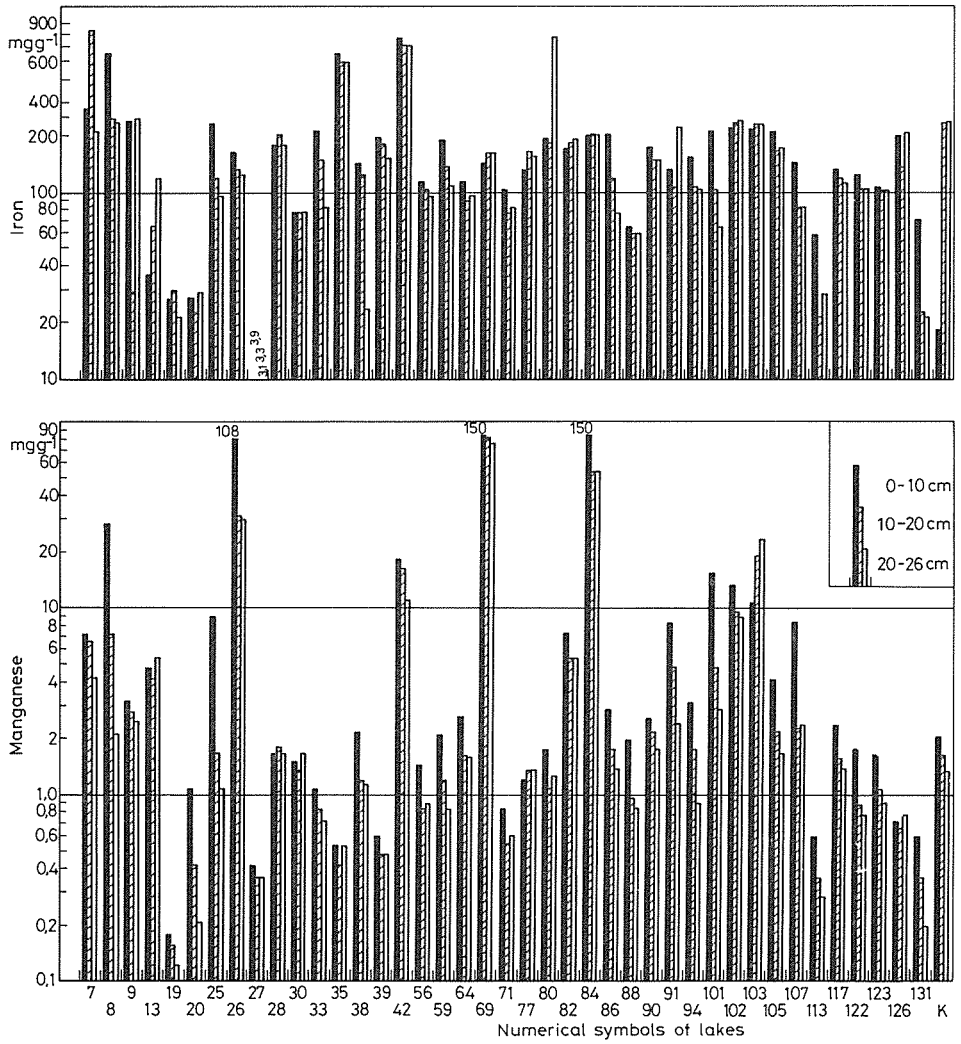

Fig. 5. Vertical distribution of iron and manganese in logaritmic scale in ash.

capable of complexing metals and increasing metal solubility, altering the distribution of oxidized and reduced forms, alleviating their toxicity and altering their availability for aquatic life, i.e. influencing the extent to which metals are adsorbed to suspended matter and affecting the stability of metal-containing colloids (Singer 1977).

In the sediments of the Kitkajärvi lakes loss on ignition depended greately on the streams and depths of the lakes (Myllymaa et al. 1985). Thus the size of the lake is a very important factor. The mean loss on ignition in the Kitkajärvi lakes was only 16 % compared with 43 % in this study (Table 1). The content of organic matter content was found here to diminish with increasing depth of the lake and area of the catchment basin (Table 2).

The rate of sedimentation depends on hydrological factors and such features as the incidence of digging in the catchment area, and in turn affects

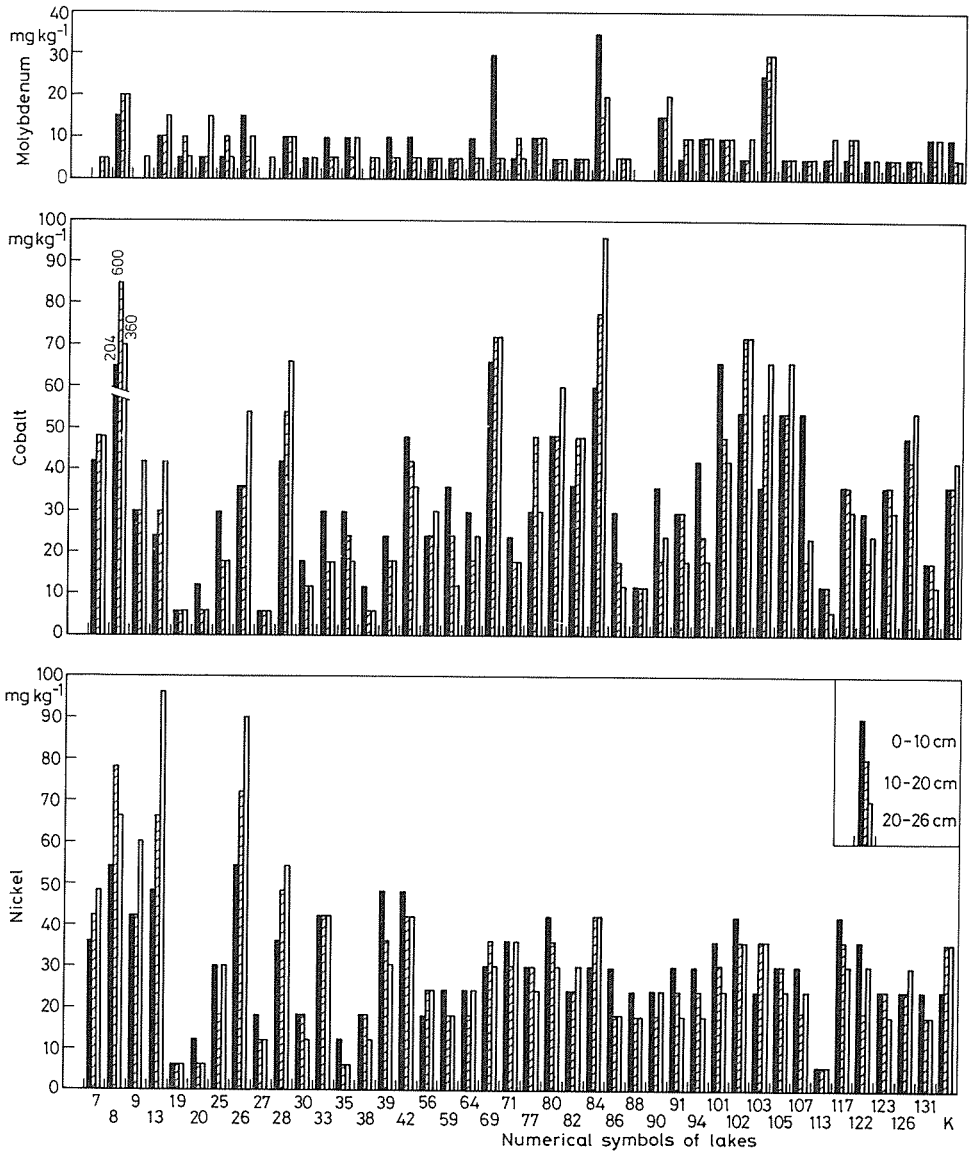

Fig. 6. Vertical distribution of molybdenum, cobalt and nickel in ash.

the sedimentation and concentration of metals, which are normally contained in the organic matter.

pH, which was quite high throughout this study, affects the precipitation and solution of metals. The pH in the sediments depended on the organic matter content and thus on the area of the catchment basin. The highest values were found in the catchment basins overlain by till deposits and basic rocks, where the buffer capacity is good. Since pH was measured in the laboratory, the values may have altered due to the oxidizing of sulphides, for instance (cf. Tolonen 1983). Thus the values cannot be regarded as entirely correct.

4.2 Nitrogen and phosphorus

The concentration of nitrogen, which is indicative of organic matter content was more than twice that found in Lake Ala-Kitka (7.2 mg g^{-1}; Myllymaa et al. 1985) and the lakes studied by the National Board of Waters (1971).

The phosphorus concentration in Lake Ala-Kitka was 1.2 mg g^{-1} of dry matter (Myllymaa et al. 1985), a figure of 1.8 mg g^{-1} being recorded for certain other major lakes in Kuusamo (National Board of Waters 1971).

The ability of sediments to bind phosphorus depends greately on the redox potential and thus on the precipitation of ferric hydroxide. Thus the high enrichment of phosphorus in the upper parts of the sediments indicates low redox potential in the sediments. The low concentration in the upper part may indicate that the oxygen balance of the lake has deteriorated. There was nevertheless no correlation between phosphorus and iron here, although phosphorus was correlated with manganese (Table 2). The differences may also be caused by changes in the runoff water. As phosphorus is not in a stable state, no adequate conclusions can be drawn on this basis (Granberg & Hakkari 1980). Phosphorus can be used as a predictor of redox potential and thus for drawing conclusions regarding the vertical distribution of metals.

4.3 Metals

4.31 Lead

Lead is released into water at low pH (Davis et al. 1982), but since pH here was generally high (mean 6.0), no correlation was between it and lead. Lead has been found to bind to oxidated sediments (Gorham and Swaine 1965), and allows conclusions to be drawn on the succession in redox potential.

The pronounced enrichment of lead in the upper parts of the sediment may be caused by complex organic or inorganic compounds, the stability of lead compounds in sediments ensuring that the differences are not smoothed out by diffusion (Tenhola 1983).

The average concentration of lead was almost equal to those reported in the lakes of Northern Karelia by Tenhola and Lummaa (1979; 28 mg kg^{-1}) and Tanskanen (1979; 40 mg kg^{-1}). The value presented by Coker and Nichol (1976) is lower (14 mg kg^{-1}). The concentration in dry matter was almost equal to that in Lake Yli-Kitka (16 mg kg^{-1}; Myllymaa et al. 1985). The highest values may be of natural or human origin, and their causes should be studied.

The main lithological sources of lead are sulphide minerals (Lahermo et al. 1979), and these could have caused the exceptional values found here, but an anthropogenic effect may be implicated, since Salminen (1979) reports high concentrations (60—143 kg^{-1}) near main roads, boat jetties and harbours.

4.32 Copper

The decline in copper towards the uppermost layer was not due to changes in redox potential, as iron and manganese did not behave in the same way in these lakes (Fig. 5). In the lakes of Northern Karelia, Fe and Mn as well as Ni, Co, Cu, Zn and Pb were enriched in the oxidized part of the sediment cores (Tenhola 1983).

The average concentration of copper was slightly greater than the figures presented by Tenhola and Lummaa (1979; 41.3 mg kg^{-1}) or Tanskanen (1979; 45 mg kg^{-1}). The concentration in dry matter was also greater than in Lake Yli-Kitka (25 mg kg^{-1}) as reported by Myllymaa et al. (1985). The concentrations were very high throughout this study in some lakes.

The appearance of copper with zinc, mercury and cobalt suggests that these metals had all been mobilised from sulphide minerals.

4.33 Zinc

Tenhola (1983) reports the concentrations of certain elements, especially that of zinc to diminished towards the surface as a rule, as a result of their solution in water. According to Sandman and Simola (1983), zinc may be considered an indicator of an anthropogenic effect, as its natural concentrations are usually low. But according to Sauvonsaari

et al. (1979) the ratio of heavy metals nearly always observes a known geochemical order, and iron, manganese and zinc occur very generally in the sediments of Finnish watercourses.

The highest values were consistently found here in the southwest part of the area, where the bedrock consists mainly of granite gneiss, although the highest average concentration in any sediment core was found in lake no. 13 (Fig. 2), where zinc and mercury values were high also in water (Myllymaa 1985). Sulphide minerals may be the source of this high zinc content.

According to Tenhola and Lummaa (1979) the size of a lake affects the zinc concentrations in its sediments the mean content in the small lakes, length > 200 m (206.1 mg kg^{-1} of ash), being twice that (95.7 mg kg^{-1}) in the large ones (> 1 000 m). The mean for the total data was 145.3 mg kg^{-1}. Also in Kuusamo, the mean value for the large Kitka lakes (60 mg kg^{-1}; Myllymaa et al. 1985) was lower than that in the smaller lakes studied here (90 mg kg^{-1}).

Zinc and cobalt concentrations usually follow those of manganese, since they are precipitated or dissolved with it in natural waters (Rankama and Sahama 1950, Kontas 1979, Tuokko 1980). This was not the case here, however (Figs. 4—5), as zinc correlated only with loss on ignition, Pb, Cd and Ni (Table 2) and seemed to be dependent more on organic matter than on Fe-Mn precipitates. The highest mean content (182.3 mg kg^{-1}) was in soil class 3, till and peat, the difference with respect to class 1 (mean 103.6 mg kg^{-1}) being almost significant.

4.34 Cadmium

The highest concentrations were found in lakes nos. 13, 26 and 80 (Figs. 2 and 4). Lake no. 13, also had high concentrations of Hg, Zn and Cu (Fig. 4), and the Zn concentration was high. Cadmium is known to be bound to carbonates and sulphide minerals along with zinc. Lake no. 26 is situated near a known deposit of sulphide ores (Myllymaa 1985).

The cadmium values found here were usually quite small (mean 0.32 mg kg^{-1}) perhaps due to the minor extent of the anthropogenic effect. Tummavuori and Aho (1978) report a mean concentration of 2.45 mg kg^{-1} of dry matter in the sediments in Central Finland, while the maximum concentration reported in Lake Yli-Kitka was 1.0 mg kg^{-1}. The average concentration in Lake Washington and Sartis Reservoir in North-America was 0.4 mg kg^{-1} (Price and Knight 1978). Finnish rocks contain more cadmium than magmatic rocks as a rule (0.3—0.4 mg kg^{-1}; Tummavuori and Aho 1978).

4.35 Mercury

Håkanson (1974) reports that mercury accumulates in the surface layer of sediments, from where it may be released back into the water and into the circulation. In weakly reduced conditions its solubility may increase again. According to the present correlations (Table 2), mercury seemed to be bound in mostly acidic lakes (cf. Rekolainen et al. 1986). This could be due to the effective sedimentation of humic substances in acidic lakes or to the low rate of decomposition of organic matter in sediments with low pH values.

Due to the small number of samples, the negative correlations of mercury with loss on ignition and nitrogen were weak (Table 2). Mercury is most strongly bound to inorganic material at pH 7 (Leskinen & Lindqvist 1982), and the lower the pH, the greater is the proportion of mercury contained in organic matter. The highest mercury concentration was found here in the area where soil was composed of till and the proportion of inorganic matter in the lake sediments was greatest.

The mercury concentrations obtained here (mean 0.14 mg kg^{-1}) were a little higher than those in Yli-Kitka (0.05 mg kg^{-1}; Myllymaa et al. 1985), while Rekolainen et al. (1986) report concentrations in the range 0.17—0.55 mg kg^{-1} in surface sediment layers in southern and western Finland and 0.02—0.05 mg kg^{-1} in Lapland. The background content was in the range 0.05—0.25 mg kg^{-1}. It is obvious that in some cases the 30—40 cm sediment core was not enough to reach the strata with the lowest mercury values (Rekolainen et al. 1986).

Earlier investigations have shown mercury concentration in the sediments of the polyhumic Lake Oijärvi (0—31 cm) to vary in the range 0.03—0.09 mg kg^{-1}, the maximum being at a depth 19—21 cm. The range observed in a eutrophic bay of this lake was 0.03—0.26 mg kg^{-1} at a depth of 26—28 cm.

The highest concentrations found here were in lakes nos. 8, 13, 90 and 94 (Fig. 4), while Myllymaa (1985) reports the highest mercury concentration in water in this same lake no. 8. There was no vertical difference, so that this could not have been caused by human agency, but lake no. 8 is situated in a catchment basin with a greenstone bedrock (cf. Silvennoinen 1972), while lake no. 13 is situated in an area where the main rock species are mica schists. The catchment areas of lakes nos. 90 and 94 contain mainly granite gneiss. The reason for

the high concentrations is unknown, but they may be caused by a sulphidic minerals.

4.36 Iron and manganese

The chemical reactions of iron and manganese are very similar, although the oxidates of manganese precipitate and dissolve at a higher redoxpotential than those of iron. Thus the Fe/Mn ratio increases in reducing conditions (Simola 1983).

The range of the Fe/Mn ratio recorded here was 1—619, the mean being 87. In most lakes the ratio was same throughout the profile or diminished towards the surface. Thus conditions may be assumed to have mostly remained stable. The greatest change was in the sediment of lake no. 33 (Figs. 2 and 5) where the ratio increased from 117 to 200 towards the surface. In lake no. 80 it was 619 in the lowermost layer but only 114 in the uppermost layer.

The Fe/Mn ratio correlated with loss on ignition (Table 2). Iron and manganese have evidently become enriched in the uppermost layers of the sediments, manganese more so than iron (Fig. 5). Iron is much less easily maintained in a reduced, mobile condition than is manganese, and appears not to be lost at overturn in the same way as manganese (Gorham 1964).

The mean concentrations of iron in ash were consistently much higher than that in the report of Tenhola and Lummaa (1979; 2.0 mg g^{-1}), whereas the concentration relation to dry matter (6.1 mg g^{-1}) was only a little higher than that in Lake Kitkajärvi (5.4 mg g^{-1}; Myllymaa et al. 1985). The manganese concentration was seven times the mean value (1.3 mg g^{-1}) reported by Tenhola and Lummaa (1979).

The high manganese and iron concentrations in these sediments are perhaps due to the ultramafic rocks, for even the dykes, liable to cause high iron concentrations.

4.37 Molybdenum

The concentrations of molybdenum did not vary much vertically (Fig. 6), although two lakes (nos. 69 and 84; Fig. 1) had high molybdenum and manganese values in their uppermost layers (Figs. 5—6). Molybdenum follows manganese, as is to be expected geologically and is thus concentrated in the surface oxidized mud (Goldsmidt 1954, ref. Gorham 1964), from where it may migrate into the water.

Like iron, copper, zinc, lead, mercury, nickel and cobalt, molybdenum precipitates in the form of sulphides upon the reduction of its sulphate (Salomons and Förstner 1984). Thus it is present in pyrite (FeS_2) as a minor metal. Molybdenum is usually concentrated in the felsic (silicious) parts of intrusive rocks. The hydroxides of manganese readily absorb molybdenum, which may explain the exceptional vertical distribution in lakes nos. 69 and 84 (Figs. 2 and 6).

4.38 Cobalt

Many of the lakes had high cobalt concentrations (Fig. 6), including anomalous high values in lake no. 8 (Ruoppilampi; Fig. 2), the catchment area of which overlies greenstones and relatively high values in lakes nos. 69, 84 and 103, where molybdenum concentrations were also high (Fig. 6). These metals precipitate in the same way as sulphides and with manganese (Salomons and Förstner 1984). Cobalt has often become enriched in ultramafic rocks along with magnesium. Lakes 69 and 84 had the highest pH recorded here (Fig. 3).

Some other metals as well as cobalt were identified in Lake Ruoppilampi (no. 8), suggesting the presence of ore minerals. Many mineralisations of cobalt, copper and gold have been found in the area studied (Pankka and Vanhanen 1984), and these may be the cause of the high levels of cobalt in the sediments. Cobalt may be a good indicator of other metals for prospecting purposes. Its mean concentration here was higher than those presented by Tenhola and Lummaa (1979; 21 mg kg^{-1} of ash) or Tanskanen (1979) for the lakes of Northern Karelia, or those reported in Superior province in Canada (12 mg kg^{-1}; Coker and Nichol 1975).

4.39 Nickel

The mean concentration of nickel obtained here is much lower than the values presented by Coker and Nichol (1976; 60 mg kg^{-1}), Tanskanen (1979; 74 mg kg^{-1}) or Tenhola and Lummaa (1979; 42.7 mg kg^{-1}). Some high values, especially in conjuction with other metals, suggest mineralisations, and thus the catchment areas should be borne in mind for prospecting purposes.

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TIIVISTELMÄ

Tutkimuksen tarkoituksena oli selvittää ravinteiden ja metallien esiintymistä pienehköjen järvien sedimenteissä sekä vertikaalisten ja alueellisten erojen syitä. Tutkitut järvet oletettiin suhteellisen luonnontilaisiksi. Niihin ei kohdistunut suoraa jätevesikuormitusta, mutta ihmisen vaikutus on mahdollista ilman kautta tapahtuneen leviämisen ja valuma-alueella tapahtuneen toiminnan vuoksi. Alueen kallioperä on vaihtelevaa. Se kuuluu suurelta osin karjalaiseen liuskevyöhykkeeseen, mutta osa alueesta kuuluu gneissigraniittialueeseen. Sekä liuske- että gneissigraniittialueilla esiintyy runsaasti emäksisiä kivilajeja, jotka vaikuttavat järvien veden ja sedimenttien laatuun. Sulfidimalmiesiintymät aiheuttavat geokemiallisia anomalioita, joita voidaan käyttää hyväksi malminetsinnässä.

Orgaanisen aineen osuus sedimentissä väheni syvyyden ja valuma-alueen kasvaessa. Kahdesta järvestä tehdyn lyijyajoituksen perusteella arvioituna sedimentaatio on ollut keskimäärin 15—17 mg cm^{-2} a^{-1} kuivapainona viimeisten sadan vuoden aikana. Tämä vastaa 2.3—2.4 mm:n vuotuista kasvua. Sedimentin pH riippuu orgaanisen aineen määrästä ja siten myös valuma-alueen laajuudesta. Korkeimmat keskiarvot olivat alueilla, joiden maaperä oli pääasiassa moreenia ja kallioperä emäksisiä kivilajeja.

Kokonaistyppi on sitoutunut orgaaniseen ainekseen ja korreloi siten järven syvyyden, valuma-alueen pinta-alan ja pH:n kanssa. Fosfori taas korreloi kokonaissyvyyden kanssa. Raudan kanssa fosfori ei korreloinut mutta mangaanin kanssa korrelaatio oli erittäin merkitsevä ja hehkutushäviön kanssa merkitsevä ja negatiivinen. Suurimmat fosforipitoisuudet olivat moreenialueiden järvissä.

Lyijyn vertikaaliset pitoisuuserot olivat suuret, ja suurimmat arvot olivat pintaosassa. Lyijy oli sitoutunut eniten orgaaniseen ainekseen. Se korreloi erittäin merkitsevästi myös sinkin ja kadmiumin kanssa sekä merkitsevästi (negatiivisesti) valuma-alueen pinta-alan kanssa. Syynä eräisiin korkeisiin arvoihin ovat ilmeisesti sulfidimineraalit, mutta ihmisen vaikutus on hyvin mahdollinen pintaosassa olevien suurten pitoisuuksien selittäjänä.

Kuparin pitoisuudet kasvoivat eräissä järvissä pintaa kohti. Tätä ei voi selittää täysin redokspotentiaalin muutoksella, koska rauta ja mangaani eivät käyttäytyneet samalla tavalla. Eräissä järvissä oli niin korkeita kuparipitoisuuksia, että syyksi voidaan epäillä malmiesiintymiä. Tällöin myös koboltin ja eräissä järvissä sinkin ja elohopean pitoisuudet olivat poikkeuksellisen suuret. Kupari korreloi erittäin merkitsevästi elohopean, molybdeenin, koboltin ja nikkelin kanssa. Suurimmat kuparipitoisuudet olivat emäksisten kivilajien alueilla.

Sinkkipitoisuus kasvoi yleensä pintaa kohti, missä vaihtelu oli suuri. Syynä korkeisiin sinkin, kuten elohopean ja kadmiumin pitoisuuksiin voi sulfidimineraalien lisäksi olla ihmisen vaikutus. Sinkin pitoisuus kasvaa yleensä järven koon pienetessä. Vaikka sinkin tiedetään yleensä seuraavan mangaania ja sitoutuvan mangaanisaostumiin, tässä tutkimuksessa sitä ei havaittu. Sinkin todettiin olevan sitoutunut lähinnä orgaaniseen ainekseen. Erittäin merkitsevä korrelaatio oli lyijyn, kadmiumin ja nikkelin kanssa. Eniten sinkkiä oli keskimäärin alueilla, joiden maaperä koostui moreenista ja turpeesta.

Myös kadmiumin pitoisuus kasvoi yleensä pintaa kohti. Ero kerrosten välillä oli erittäin merkitsevä. Järvissä, joiden sedimentin kadmiumpitoisuus oli suuri, tavattiin suurina pitoisuuksina myös elohopeaa, sinkkiä ja kuparia, mikä viittaa malmiesiintymien vaikutukseen. Kadmiumin pitoisuudet olivat yleensä pienet, mikä viittaa vähäiseen ihmistoiminnan vaikutukseen. Erittäin merkitsevä korrelaatio kadmiumilla oli hehkutushäviön, lyijyn, sinkin ja nikkelin kanssa. Suurimmat pitoisuudet olivat moreenialueilla.

Elohopeapitoisuus nousi yleensä pintaa kohti. Järvien välillä ei ollut suurta eroa. Kahdessa järvessä, joista tehtiin lyijyajoitus, suurin lisäys on tapahtunut 50—70 vuotta sitten, jolloin myös sedimentaatio on ollut nopeinta. Tutkittujen järvien veden ja sedimenttien pH oli korkea, mistä johtuen elohopea oli sitoutunut lähinnä epäorgaaniseen ainekseen, ja pH:n kanssa sillä oli erittäin merkitsevä positiivinen korrelaatio. Korrelaatio oli erittäin merkitsevä myös kuparin, molybdeenin, koboltin ja nikkelin kanssa. On mahdollista, että elohopean esiintyminen joissakin järvissä poikkeavan suurina pitoisuuksina johtuu sulfidimineraaleista, mutta myös ihmisen vaikutus oli yleisesti näkyvissä elohopean gradientissa. Selvästi suurin pitoisuus oli

Ruoppilammessa, jonka vedestäkin on havaittu korkeita pitoisuuksia. Tässä sedimentissä ei ollut vertikaalista eroa, joten suuren määrän voidaan olettaa johtuvan kallioperän mineraaleista. Kallioperä koostuu pääasiassa emäksisistä vihreäkivistä.

Useimmissa järvissä rauta-mangaanisuhde oli vertikaalisesti lähes vakio, joten redokspotentiaali oli pysynyt muuttumattomana. Orgaanisen aineksen osuus vaikuttaa tähän suhteeseen, joten korrelaatio haihdutushäviön kanssa oli erittäin merkitsevä. Rauta ja varsinkin mangaani olivat rikastuneet sedimentin yläosaan. Suurten rauta- ja mangaanipitoisuuksien arvellaan johtuvan ultramafisista kivilajeista. Rauta korreloi tässä tutkimuksessa merkitsevästi pelkästään järviprosentin ja heikosti koboltin kanssa. Mangaani korreloi positiivisesti järven syvyyden, pH:n, fosforin ja molybdeenin sekä negatiivisesti haihdutushäviön ja typen kanssa.

Molybdeenin pitoisuus ei yleensä vaihdellut vertikaalisesti. Kahden järven sedimentin pintaosan pitoisuus oli korkea ja johtui molybdeenin siirtymisestä hapekkaaseen pintaosaan mangaanin kanssa. Molybdeeni korreloi negatiivisesti typen sekä positiivisesti fosforin, sinkin, kuparin, mangaanin, koboltin ja nikkelin kanssa. Sulfidimalmit sisältävät yleisesti molybdeeniä, rautaa, kuparia, sinkkiä, elohopeaa, nikkeliä ja kobolttia ja voivat olla tärkeä molybdeenin lähde tällä alueella.

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